

Enthalpy of dissociation and hydration number of methane hydrate from the Clapeyron equation

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Abstract

The enthalpies of the reactions in which methane hydrate is dissociated to methane vapor and either (1) water, or (2) ice are determined by a new analysis using the Clapeyron equation. The difference in enthalpies of the two reactions is used to infer the hydration number at the quadruple point where hydrate, ice, liquid water, and methane vapor coexist. By appropriate corrections, the hydration number at points removed from the quadruple point is also determined. The most important feature of the new analysis is the direct use of the Clapeyron equation. The method avoids the use of certain simplifying assumptions that have compromised the accuracy of previous analyses in which the Clausius–Clapeyron equation was used. The analysis takes into account the finite volumes of all phases, the non-ideality of the vapor phase, and the solubility of methane in water. The results show that the enthalpy of dissociation and hydration number are constant within experimental error over the entire (hydrate, liquid, vapor) coexistence region. The results are more accurate than but entirely consistent with almost all previous studies.

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1. Introduction

Interest in the class of compounds known as gas hydrates has been increasing in recent years. Methane hydrate sometimes forms as an unwanted guest in gas pipelines. Naturally occurring methane hydrate plays an important role in the terrestrial carbon balance, and is being considered as a potential resource for energy production. For these reasons methane hydrate has been extensively studied. Even so, there is some controversy about its basic properties. For example, theory suggests that hydration numbers in the range of 5.75 to approximately 8.0 might result in a stable hydrate. Pre-

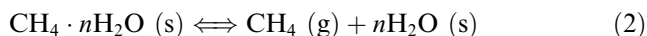
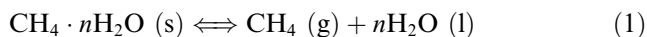
vious studies have given results that span this rather wide range. However, most previous studies were unable to indicate how the hydration number might vary with the temperature and pressure at which the hydrate was formed. This work gives results for the hydration number and enthalpy of dissociation over a wide range of temperatures and pressures.

We use an improvement of an old technique [1] for determining the enthalpies of dissociation and hydration number for the dissociation of solid hydrate to gaseous methane and (1) liquid water, or (2) ice. The improved method is described in a recent paper by the author [2] in which the hydration number and the enthalpy of dissociation of carbon dioxide hydrate were determined. Methane hydrate, because it exists over a wider range of temperature and pressure than carbon dioxide hydrate, requires more refinements in the analysis.

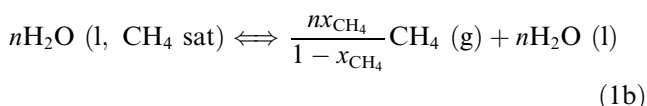
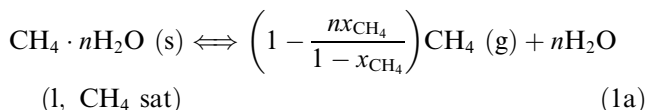
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2. Method of analysis

The following two equations represent the dissociation of methane hydrate to gaseous methane and liquid water, and gaseous methane and ice, respectively.



All enthalpy changes in this work are based on the dissociation of hydrate to form one mole of methane vapor, and an initially unknown number of moles of either water or ice. We will determine ΔH_1 and ΔH_2 from an analysis of the (p, T) behavior along the (liquid, hydrate, vapor) and (ice, hydrate, vapor) equilibrium lines. There is a small complication with regard to reaction (1), however. The liquid in equilibrium with hydrate is not pure water; rather it is water that is saturated with respect to methane at the appropriate temperature and pressure. A non-negligible fraction of the methane released in reaction (1) goes into the liquid phase. Suppose that the mole fraction of methane in the water in equilibrium with the hydrate is x_{CH_4} . Then n moles of water supplies $nx_{\text{CH}_4}/(1 - x_{\text{CH}_4})$ moles of methane to the hydrate; the rest comes from the gas. Thus reaction (1) must be analyzed as the sum of two terms:



$$\Delta H_1 = \Delta H_{1a} + \Delta H_{1b}. \quad (3)$$

The term $\text{H}_2\text{O (l, CH}_4 \text{ sat)}$ refers to a mole of liquid water which is saturated with respect to methane at the given temperature and pressure. The Clapeyron equation will be used to find ΔH_{1a} , while solubility data will be used to find ΔH_{1b} . There is no analogous complication in determining ΔH_2 because the solubility of methane in ice is negligible.

de Forcrand [1] showed that if accurate values for ΔH_1 and ΔH_2 were known in the vicinity of quadruple point Q1, where both reactions can occur simultaneously, it would be an easy matter to determine $n(\text{Q1})$ since the difference between reactions (1) and (2) represents the freezing of n moles of water, whose enthalpy change per mole is known. If adequate physical properties of the reactants are known, the reaction enthalpies can be corrected for temperature and pressure. The method can then be extended to determine n at temperatures and pressures away from quadruple point Q1.

The Clapeyron equation relates the enthalpy change of a phase-equilibrium reaction to the volumetric properties of the reactants and products along the phase boundary. We present it without derivation.

$$\Delta H = T\Delta V(dp/dT), \quad (4)$$

where ΔV is the volume changes that take place due to the phase change. The ΔV term is the part of the Clapeyron equation that presents the most difficulty. As temperature increases over the stability field of the hydrate, dp/dT becomes very large and ΔV becomes correspondingly very small. It is necessary to find accurate representations of the volumes of each of the phases in equilibrium, and to account for how these vary with temperature and pressure.

We begin by analysis of reaction (2), because it is straightforward and because the value of ΔH_2 will be required in order to find ΔH_1 and n .

2.1. Method for determining the enthalpy of dissociation of hydrate to methane vapor and ice (reaction (2))

The (p, T) data used in this work were taken from tables given by Sloan [3], who compiled data from several sources. The data sets that were used in this work are summarized in table 1.

The (p, T) data are plotted as $\ln(p/\text{MPa})$ vs. K/T in figure 1.

The data are least-squares fitted to a third order polynomial in $1/T$.

$$\ln(p^{\text{IHV}}/\text{MPa}) = a_0 + a_1\left(\frac{K}{T}\right) + a_2\left(\frac{K}{T}\right)^2. \quad (5)$$

This fitting function represents the data extremely well and is easily differentiated with respect to $1/T$.

$$\frac{d \ln(p^{\text{IHV}}/\text{MPa})}{d(K/T)} = a_1 + 2a_2\left(\frac{K}{T}\right). \quad (6)$$

Finally dp/dT is found by the identity

$$\frac{dp}{dt} \equiv \frac{-(p)}{T^2} \frac{d \ln(p)}{d(1/T)}. \quad (7)$$

The fit parameters are given in table 2.

The volume change for reaction (2) is given by

TABLE 1
Sources of (P, T) data along the (ice, hydrate, vapor) coexistence line for methane hydrate

Source
Roberts <i>et al.</i> [4]
Falabella [5]
Deaton and Frost [6]
Makogon and Sloan [7]

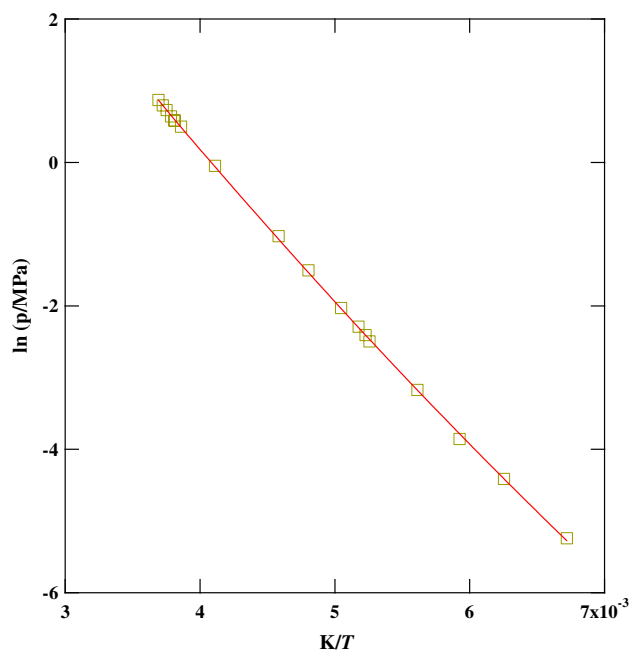


FIGURE 1. (p, T) data along the (ice, hydrate, vapor) coexistence line for methane hydrate. \square , data points; —, third-order polynomial fit.

TABLE 2

Fit parameters for equations (5) and (6)

Parameter	Value
a_0	10.075
a_1	−2750.3
a_2	69345

$$\Delta V_2 = (\text{volume of } n \text{ moles ice}) + (\text{volume of 1 mole methane vapor}) - (\text{volume of hydrate containing 1 mole methane}) = nV_{\text{ice}} + V_{\text{CH}_4} - V_{\text{hyd}}. \quad (8)$$

The hydrate volume is found from neutron diffraction studies of Klapproth *et al.* [8] They found that the zero-pressure intercept of the lattice parameter for methane hydrate is $a = 1.1955$ nm. The volume of a mole of unit cells at low pressure is thus

$$V_{\text{unit}}/(\text{m}^3 \cdot \text{mol}^{-1}) = (1.1955 \cdot 10^{-9})^3 (6.022 \cdot 10^{23}) = 1.0290 \cdot 10^{-3}. \quad (9)$$

Each unit cell for an SI type hydrate contains 46 molecules of water and $46/n$ molecules of methane. Thus the volume of hydrate containing one mole of methane is

$$V_{\text{hyd}}/(\text{m}^3 \cdot \text{mol}^{-1}) = \frac{1.0290 \cdot 10^{-3} n}{46} = 2.2369 \cdot 10^{-5} n. \quad (10)$$

The CRC Handbook [30] gives the molar volume of ice at low pressure as $V_{\text{ice}} = 1.963 \cdot 10^{-5} \text{ m}^3 \cdot \text{mol}^{-1}$. Finally,

the molar volume of methane vapor is found from the equation of state for pure methane in the NIST Webbook [9]. Because of the very small mole fraction of water in the vapor phase, we neglect its effect on the vapor volume. Substituting into equation (8),

$$\Delta V_2/(\text{m}^3 \cdot \text{mol}^{-1}) = V_{\text{CH}_4}/(\text{m}^3 \cdot \text{mol}^{-1}) - 2.739 \cdot 10^{-6} \cdot n. \quad (11)$$

It will be found that the solid phases contribute a small amount to the total volume change; therefore no corrections for the effects of temperature and pressure on these quantities are necessary. For the same reason, the apparent value of ΔH_2 will not depend strongly on the value we assign to n . We anticipate a value $n = 6.0$.

2.2. Method for determining the enthalpy of dissociation of hydrate to methane vapor and liquid water (reaction (1a))

The (p, T) data along the (liquid, hydrate, vapor) coexistence line are more complex than the data along the (ice, hydrate, vapor) line. The (p, T) data were taken from tables given by Sloan [3], who compiled data from several sources. The data sets that were used in this work are summarized in table 3.

The data (90 data points in all) are shown plotted as $\ln(p)$ vs. $1/T$ in figure 2.

It was found necessary to use a sixth-order fit to adequately represent the data.

$$\ln(p^{\text{LHV}}/\text{MPa}) = \sum_{i=0}^5 b_i \left(\frac{K}{T}\right)^i. \quad (12)$$

Differentiation proceeds as in equations (6) and (7). Table 4 gives the fitting parameters.

2.3. Finding $\Delta V(T, p)$

The volume change for reaction (1a) is

TABLE 3

Sources of (p, T) data along the (liquid, hydrate, vapor) (LHV) coexistence line for methane hydrate

Source
Roberts <i>et al.</i> [4]
Marshall <i>et al.</i> [10]
Jhaveri and Robinson [11]
Galloway <i>et al.</i> [12]
Deaton and Frost [6]
Kobayashi and Katz [13]
McLeod and Campbell [14]
Verma [15]
de Roo <i>et al.</i> [16]
Thakore and Holder [17]
Adisasmitho <i>et al.</i> [18]
Makogon and Sloan [7]

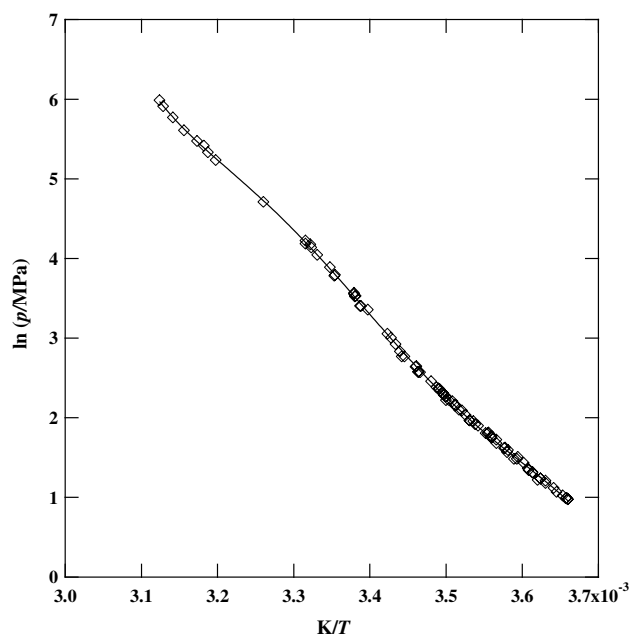


FIGURE 2. $\ln(p)$ vs. $1/T$ data along the (liquid, hydrate, vapor) coexistence line for methane hydrate. \diamond , data points; —, sixth-order polynomial fit.

TABLE 4
Fit parameters for equation (12)

Parameter	Value
b_0	$1.917598\text{E} + 5$
b_1	$-2.829261\text{E} + 8$
b_2	$1.668137\text{E} + 11$
b_3	$-4.912513\text{E} + 13$
b_4	$7.225574\text{E} + 15$
b_5	$-4.24645\text{E} + 17$

$$\Delta V_{1a} = \left(1 - \frac{nx_{\text{CH}_4}}{1 - x_{\text{CH}_4}}\right) V_{\text{CH}_4} + nV_{\text{liq}} - V_{\text{hyd}}. \quad (13)$$

The meaning of the volume terms in (13) is as follows: V_{CH_4} is the volume of 1 mole of methane vapor, V_{liq} is the volume of liquid containing 1 mole of water and $(x_{\text{CH}_4}/1 - x_{\text{CH}_4})$ moles dissolved methane and V_{hyd} is the volume of hydrate containing 1 mole of methane.

V_{CH_4} was found at each (T, p) using the methane equation of state in the NIST Webbook [9].

Equation (10) is no longer an adequate expression for V_{hyd} . Since the (liquid, hydrate, vapor) line spans a wide range of temperature and pressure, we need to account for the thermal expansion and compressibility of the hydrate crystal. To find the compressibility we again refer to the work of Klapproth *et al.* [8]. They measured the lattice parameter a of the hydrate crystal as a function of pressure at $T = 271.15$ K. The volume coefficient of compressibility κ_T (the reciprocal of the isothermal bulk modulus) was found to be

$$\kappa_T \equiv -\frac{1}{V_{\text{hyd}}} \left(\frac{\partial V_{\text{hyd}}}{\partial p} \right)_T = 1.098 \cdot 10^{-4} (\text{MPa})^{-1} \quad (14)$$

To account for thermal expansion we refer to the work of Udachin *et al.* [19]. They used X-ray diffraction to measure the lattice parameter of carbon dioxide hydrate as a function of temperature. Since carbon dioxide hydrate has SI structure and almost identical lattice parameters to methane hydrate, their results should apply reasonably well to methane hydrate. The volume coefficient of thermal expansion β found from their data is

$$\beta \equiv \frac{1}{V_{\text{hyd}}} \left(\frac{\partial V_{\text{hyd}}}{\partial T} \right)_p = 1.78 \cdot 10^{-4} \text{K}^{-1} \quad (15)$$

We use as a reference condition the Klapproth *et al.* [8] volume for methane hydrate at $p = 0$ MPa, $T = 271.15$ K (see equation (10)), then calculate the volume at other temperature and pressures from

$$\begin{aligned} V_{\text{hyd}}(T, p) / (\text{m}^3 \cdot \text{mol}^{-1}) = \\ (2.2369 \cdot 10^{-5}) \cdot (1 - 1.098 \cdot 10^{-4} \cdot p / \text{MPa}) \cdot \\ (1 + 1.78 \cdot 10^{-4} (T / \text{K} - 271.15)) \cdot n. \end{aligned} \quad (16)$$

The volume of liquid containing 1 mole of water is the sum of contributions from water and methane

$$V_{\text{liq}}(T, p) = V_{\text{H}_2\text{O}, \text{CH}_4}(T, p) + \frac{x_{\text{CH}_4}}{1 - x_{\text{CH}_4}} V_{\text{CH}_4, \text{H}_2\text{O}}(T, p). \quad (17)$$

The volumes on the right-hand side of equation (17) are partial molar quantities; in principle they depend on composition as well as temperature and pressure. However, the solubility of methane in water is so low that $V_{\text{CH}_4, \text{H}_2\text{O}}$ is essentially constant and equal to the so-called “infinite dilution” value. This quantity and its dependence on temperature and pressure is discussed in Appendix A. The partial molar volume of water, $V_{\text{H}_2\text{O}, \text{CO}_2}$, is taken to be the molar volume of pure water at (T, p) , and is calculated using the water equation of state in the NIST Webbook [9].

2.4. Method for determining the solubility and enthalpy of solution of methane in water (reaction (1b))

In reaction (1b), a saturated solution of methane containing n moles of water decomposes to methane vapor and pure water at a temperature and pressure corresponding to a point on the LHV line. We first need to calculate x_{CH_4} , the saturation mole fraction of methane, and then calculate the enthalpy change. While not straightforward, these calculations are supported by excellent experimental data and by well-validated models for adjusting the solubility and enthalpy of solution to high-pressure conditions. The calculations are detailed in Appendix A.

TABLE 5
Enthalpy change for reaction (2) from 150 K to 270 K

T/K	p/MPa	$d(p/\text{MPa})/d(T/K)$	$\frac{\Delta V_2}{(\text{m}^3 \cdot \text{mol}^{-1})}$	$\frac{\Delta H_2}{(\text{kJ} \cdot \text{mol}^{-1})}$
150	0.00564	$(4.57 \pm 0.17) \times 10^{-4}$	0.2209	15.14 ± 0.56
170	0.02463	$(1.648 \pm 0.035) \times 10^{-3}$	0.05723	16.03 ± 0.37
190	0.08380	$(4.700 \pm 0.061) \times 10^{-3}$	0.01872	16.72 ± 0.22
210	0.23475	$(1.112 \pm 0.009) \times 10^{-2}$	0.007326	17.11 ± 0.14
230	0.56442	$(2.291 \pm 0.012) \times 10^{-2}$	0.003292	17.35 ± 0.10
250	1.2012	$(4.220 \pm 0.016) \times 10^{-2}$	0.001648	17.38 ± 0.10
270	2.3162	$(7.106 \pm 0.022) \times 10^{-2}$	0.000896	17.24 ± 0.10

2.5. Summary of the method of analysis for the (liquid, hydrate, vapor) equilibrium (reaction (1))

Thus far we have outlined a method for determining $\Delta H_1(T, p)$. Using T as the independent variable, we make a table starting at $T = 274$ K and extending to $T = 318$ K, in 4 K increments. For each T , we find p , dp/dT , and ΔV_{1a} as discussed above, from which $\Delta H_{1a}(T, p)$ is found from equation (4). To this we add $\Delta H_{1b}(T, p)$ as discussed in Appendix A. Most of the calculations require a value for the hydration number n , which is initially unknown. A starting estimate of $n = 6.0$ is chosen and later refined by iteration.

2.6. Determining the hydration number at the quadruple point Q1

At the quadruple point Q1, both reactions (1) and (2) occur simultaneously. Subtracting reaction (2) from reaction (1),



The quadruple point Q1 is not far removed from standard conditions ($p^0 = 0.1013$ MPa, $T^0 = 273.15$ K), and thus the enthalpy of fusion at Q1 will be very close to the standard enthalpy of fusion of ice, $6.01 \text{ kJ} \cdot \text{mol}^{-1}$.

$$n(\text{Q1}) = \frac{[\Delta H_1(\text{Q1}) - \Delta H_2(\text{Q1})]/(\text{kJ} \cdot \text{mol}^{-1})}{6.01} \quad (19)$$

2.7. Determining the hydration number at T, p removed from Q1

The hydration number may be extended to T, p conditions removed from Q1 by standard technique in which we convert $\Delta H_1(T, p)$ to the value (denoted by ΔH^*) that it would have at Q1, where $T^* = 272.9$ K and $p^* = 2.563$ MPa. The method to perform this conversion is discussed in Appendix B.

The final equation for n is,

$$n(T, p) = \frac{[\Delta H_1^*(T, p) - \Delta H_2(\text{Q1})]/(\text{kJ} \cdot \text{mol}^{-1})}{6.01} \quad (20)$$

3. Results

Table 5 summarizes the calculation of ΔH_2 at 10 degree intervals from 150 K to 270 K.

Error analysis was complicated by the fact that the original (p, T) data do not provide uncertainties. Therefore a statistical method had to be employed. Uncertainties in the values of dp/dT were estimated at each temperature by locally fitting the p vs. T data and taking the estimated standard deviation of the slope fit coefficient. Error limits for ΔH_2 were estimated by assuming that all of the error comes from the uncertainty in dp/dT .

The results are plotted in figure 3. Also shown is an exponential fit to the data.

The least-squares fit was used to compute the value of ΔH_2 at Q1, which corresponds to $T^* = 272.9$ K, $p^* = 2.563$ MPa

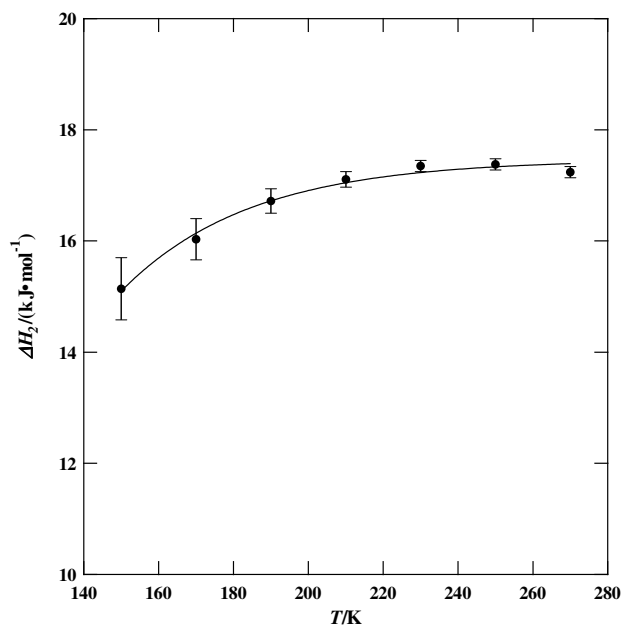


FIGURE 3. ΔH_2 vs. T . Enthalpy of dissociation of methane hydrate to methane vapor and ice.

TABLE 6
Enthalpy change of reaction (1) and hydration number from 274 K to 318 K

T/K	p/MPa	$\text{d}p/\text{d}T$ ($\text{MPa} \cdot \text{K}^{-1}$)	x_{CH_4}	ΔV ($\text{m}^3 \cdot \text{mol}^{-1}$)	$\Delta H_{1a}(T,p)$ $\text{kJ} \cdot \text{mol}^{-1}$	$\Delta H_{1b}(T,p)$ $\text{kJ} \cdot \text{mol}^{-1}$	$\Delta H_1(T,p)$ $\text{kJ} \cdot \text{mol}^{-1}$	ΔH_1^* $\text{kJ} \cdot \text{mol}^{-1}$	n
274	2.85	0.270 ± 0.007	0.00115	$7.16\text{E}-04$	52.9 ± 1.3	0.132	53.0 ± 1.3	52.9 ± 1.3	5.89 ± 0.22
278	4.28	0.414 ± 0.011	0.00146	$4.60\text{E}-04$	52.9 ± 1.4	0.158	53.1 ± 1.4	52.3 ± 1.4	5.79 ± 0.23
282	6.36	0.660 ± 0.0020	0.00181	$2.91\text{E}-04$	54.2 ± 1.5	0.185	54.4 ± 1.5	53.1 ± 1.5	5.93 ± 0.26
286	9.88	1.150 ± 0.037	0.00229	$1.69\text{E}-04$	55.5 ± 1.7	0.217	55.7 ± 1.7	54.3 ± 1.7	6.12 ± 0.28
290	16.06	2.016 ± 0.069	0.00286	$9.15\text{E}-05$	53.5 ± 1.7	0.259	53.7 ± 1.7	52.5 ± 1.7	5.83 ± 0.29
294	26.69	3.39 ± 0.12	0.00349	$5.27\text{E}-05$	52.5 ± 1.8	0.287	52.8 ± 1.8	51.8 ± 1.8	5.71 ± 0.30
298	43.92	5.31 ± 0.21	0.00419	$3.39\text{E}-05$	53.7 ± 1.9	0.294	54.0 ± 1.9	52.9 ± 1.9	5.90 ± 0.32
302	69.68	7.62 ± 0.31	0.00499	$2.36\text{E}-05$	54.2 ± 2.0	0.294	54.5 ± 2.0	53.7 ± 2.0	6.02 ± 0.34
306	105.18	10.17 ± 0.44	0.00583	$1.75\text{E}-05$	54.5 ± 2.2	0.266	54.8 ± 2.2	53.2 ± 2.2	5.94 ± 0.36
310	151.70	13.28 ± 0.60	0.00661	$1.32\text{E}-05$	54.4 ± 2.3	0.200	54.6 ± 2.3	52.6 ± 2.3	5.85 ± 0.38
314	214.40	18.74 ± 0.89	0.00723	$9.29\text{E}-06$	54.7 ± 2.4	0.081	54.7 ± 2.4	52.5 ± 2.4	5.83 ± 0.40
318	311.12	31.6 ± 1.6	0.00744	$5.45\text{E}-06$	54.7 ± 2.6	-0.114	54.6 ± 2.6	52.5 ± 2.6	5.82 ± 0.44

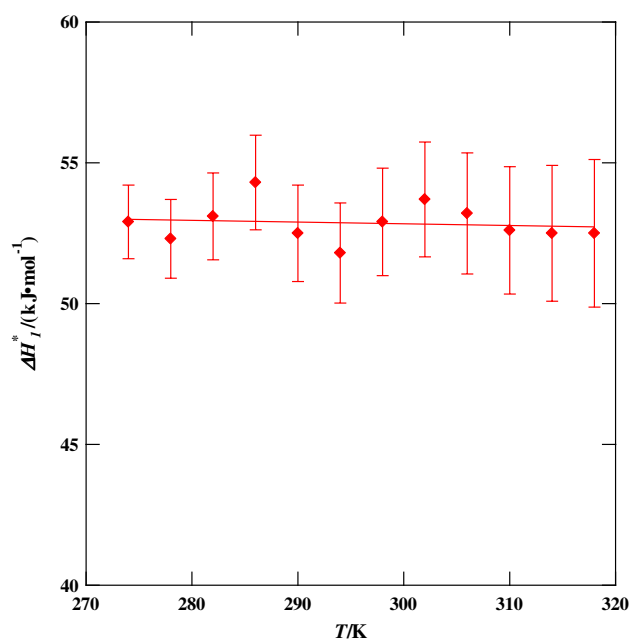


FIGURE 4. ΔH_1^* vs. T . Enthalpy of dissociation of methane hydrate to methane vapor and water, corrected to quadruple point Q1.

$$\Delta H_2(Q1)/(\text{kJ} \cdot \text{mol}^{-1}) = 17.47 \pm 0.10. \quad (21)$$

Table 6 summarizes the calculation of ΔH_1^* and n at 4 K intervals from 274 K to 318 K. An error analysis was done using the same procedure as used for reaction (2).

Figure 4 is a plot of ΔH_1^* vs. T .

Figure 5 shows how the apparent hydration number varies with T .

4. Discussion

Numerous previous investigators have determined ΔH_1 and ΔH_2 for methane hydrate using the Clapeyron equation. However, almost all of these analyses have

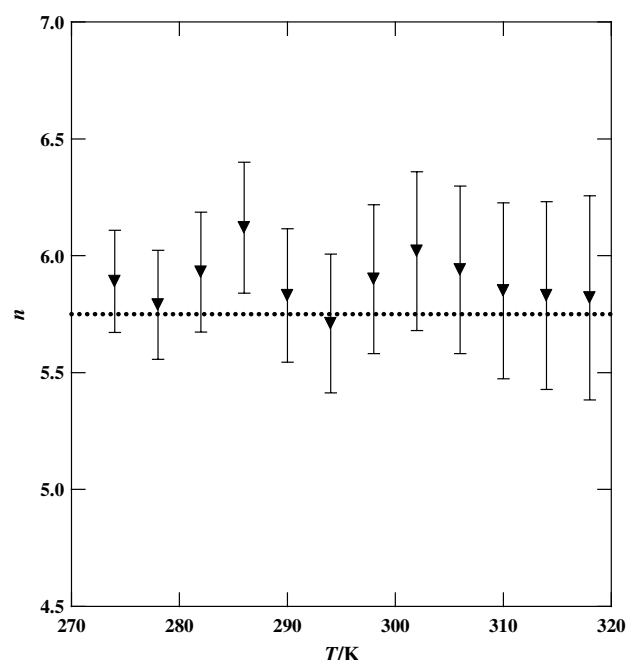


FIGURE 5. Apparent hydration number of methane hydrate vs. T . ▼, from Clapeyron analysis; ·····, minimum theoretical value for SI hydrate.

used the approximation leading to the Clausius–Clapeyron equation, namely the neglect of the volumes of the condensed phases. This approximation tends to overestimate the ΔV term in the Clapeyron equation and hence gives too large a value for ΔH . In most cases (with the exception of the results of Glew [23]) the values of ΔH are not corrected to standard conditions; presumably they are reported at the conditions of quadruple point Q1, where the de Forand method applies. Table 7 summarizes all of the known Clapeyron analyses to date for methane hydrate.

The most useful comparison of the present work is with the calorimetric study of Handa [24], who reported

TABLE 7

Comparison of present work with previous determinations of ΔH_1 and ΔH_2 for methane hydrate, evaluated at quadruple point Q1

Source	$\Delta H_1(Q1)$ (kJ · mol ⁻¹)	$\Delta H_2(Q1)$ (kJ · mol ⁻¹)
de Roo <i>et al.</i> [16]	67.85	23.37
Frost and Deaton [20]		19.06
Roberts <i>et al.</i> [21]	54.36	
Deaton and Frost [6]	55.12	
McLeod and Campbell [14]	55.07	
Marshall <i>et al.</i> [10]	53.41	
Yoon <i>et al.</i> [22]	53.81	17.53
Glew [23]	55.36	18.06
Present work	52.9 ± 1.3	17.47 ± 0.10

TABLE 8

Standard enthalpies of dissociation of methane hydrate from present work compared to calorimetric results of Handa [24]

Source	ΔH_1^0 (kJ · mol ⁻¹)	ΔH_2^0 (kJ · mol ⁻¹)
Handa [24]	54.19 ± 0.28	18.13 ± 0.27
Present work	53.5 ± 1.3	18.01 ± 0.10

values of ΔH_1^0 and ΔH_2^0 corrected to standard conditions of $p^0 = 0.1013$ MPa, $T^0 = 273.15$ K. The results of the present work were corrected to standard conditions using the methods described in Appendix B.

The enthalpies of reactions (1) and (2) are in excellent agreement with the calorimetric results (table 8). The hydration number at Q1, $n = 5.90 \pm 0.3$, also agrees with that reported by Handa, $n = 6.00 \pm 0.01$. The present method goes beyond what most of the previous studies were able to do in that it determines ΔH_1 and n at several points along the (liquid, hydrate, vapor) phase boundary. Both are seen to be essentially constant over a 44 K temperature range and a hundred-fold increase of pressure. The only other study of methane hydrate that attempts to calculate enthalpies and hydration numbers as a continuous function of temperature is the study of Glew [23]. His results for hydration number agree with the present results within experimental error over most of the temperature range. His results for the enthalpy of dissociation are between 5% and 10% larger than the present results and show a definite trend with temperature, in contrast to the present results. The discrepancy between the present results and those of Glew [23] are unclear but might be due to differing methods for determining the molar volume of the hydrate. This has a large effect on the results when using the Clapeyron equation. Regardless of which result is closer to the truth, it is clear that the structure and energetics of methane hydrate have at most a small variation over a wide range of temperatures and pressures. This is a testament to the extraordinary stability of methane hydrate, which in turn no doubt derives from the fact

that the methane molecule is a good fit to both small and large cages in the SI structure. Methane hydrate differs in this respect from carbon dioxide hydrate, for which a previous study [2] shows that the cage filling varies significantly with temperature and pressure.

5. Conclusions

A method is outlined for determining the enthalpy of dissociation of methane hydrate using the rigorous Clapeyron equation. Most of the previous determinations are flawed by the use of the Clausius–Clapeyron equation. The Clausius–Clapeyron equation may give an approximately correct answer for some gas hydrates at low pressure, for which the underlying assumptions are nearly valid. For high-pressure systems such as methane hydrate, however, and especially at temperatures far from the lower quadruple point, a more rigorous approach is required. To fully exploit the rigor of the Clapeyron equation, a large amount of supplemental data for hydrate systems is required. This includes solubility of the guest gas in water, and several state properties of the hydrate, including density, bulk modulus, thermal expansion coefficient, and heat capacity. The methods for incorporating these properties in the Clapeyron analysis are described in this work.

Methane hydrate is a severe test of the Clapeyron equation because of the very high pressures at which it exists. However, it is also a hydrate for which a variety of physical properties have been measured accurately. The net result is a very satisfactory analysis whose results are in accord with almost all previous studies. For most other gas hydrates, which exist at pressures much lower than that of methane hydrate, the method outlined here is also expected to work extremely well.

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Appendix A. Solubility and enthalpy of solution of CH₄ in water on the (liquid, hydrate, vapor) three-phase coexistence curve

The finite solubility of CH₄ in water and the enthalpy of solution affect the Clapeyron analysis of the hydrate dissociation enthalpy in several ways, as discussed in the text. The solubility may be determined from readily

available data using the Krichevsky–Kasarnovsky [25] equation,

$$\ln(f/x_{\text{CH}_4}) = \ln K_{\text{H}} + \frac{V_{\text{CH}_4, \text{H}_2\text{O}}^{\infty}(p - p^s)}{RT} \quad (\text{A.1})$$

The terms in equation (A.1) are as follows: f , fugacity of CH_4 in the gas phase; x_{CH_4} , mole fraction of CH_4 dissolved in the liquid phase; K_{H} , Henry's law constant; $V_{\text{CH}_4, \text{H}_2\text{O}}^{\infty}$, partial molar volume of CH_4 in water at infinite dilution; p , total system pressure; p^s , vapor pressure of the solvent (water) at temperature T .

Dhima *et al.* [26] demonstrated the validity of the K–K equation for high-pressure aqueous solutions of several gases, including CH_4 . Rettich *et al.* [27] have accurately measured K_{H} and $V_{\text{CH}_4, \text{H}_2\text{O}}^{\infty}$. The partial molar volume at infinite dilution is independent of pressure and only slightly dependent on temperature.

$$\ln[V_{\text{CH}_4, \text{H}_2\text{O}}^{\infty}/(\text{m}^3 \cdot \text{mol}^{-1})] = -10.275 + 1.23 \cdot 10^{-3}(T/\text{K} - 273.15). \quad (\text{A.2})$$

In evaluating the fugacity it is assumed that the gas is pure methane, whose equation of state is found in the NIST webbook [9]. The methane solubility found by the procedure outlined above is given in figure 6. Also shown are measured values due to Servio and Englezos [28].

Because the mole fraction x_{CH_4} is so low, the enthalpy of solution per mole of methane can be equated with little error to the partial molar enthalpy of solution at infinite dilution, which we denote by $\Delta H_{\text{CH}_4, \text{H}_2\text{O}}^{\infty}$. Benson and Krause [29] give the following formula for determining this quantity, assuming only that $V_{\text{CH}_4, \text{H}_2\text{O}}^{\infty}$ is independent of pressure;

$$\Delta H_{\text{CH}_4, \text{H}_2\text{O}}^{\infty} = R \frac{d \ln K_{\text{H}}}{d(1/T)} - T \frac{dV_{\text{CH}_4, \text{H}_2\text{O}}^{\infty}}{dT}(p - p^s) + V_{\text{CH}_4, \text{H}_2\text{O}}^{\infty}(p - p^s) + TV_{\text{CH}_4, \text{H}_2\text{O}}^{\infty} \frac{dp^s}{dT}. \quad (\text{A.3})$$

TABLE A.1
Enthalpy change of reaction (1b)

T/K	p/MPa	x_{CH_4}	$R \frac{d \ln K_{\text{H}}}{d(1/T)}$ ($\text{kJ} \cdot \text{mol}^{-1}$)	$V_{\text{CH}_4}^{\infty}(p - p^s)$ ($\text{kJ} \cdot \text{mol}^{-1}$)	$\Delta H_{\text{CH}_4, \text{H}_2\text{O}}^{\infty}$ ($\text{kJ} \cdot \text{mol}^{-1}$)	$\Delta H_{1\text{b}} = -\frac{nx_{\text{CH}_4}}{1-x_{\text{CH}_4}} \Delta H_{\text{CH}_4, \text{H}_2\text{O}}^{\infty}$ ($\text{kJ} \cdot \text{mol}^{-1}$)
274	2.8490	0.001146	−19.313	0.098	−19.215	0.132
278	4.2810	0.001455	−18.219	0.149	−18.070	0.158
282	6.3640	0.001813	−17.157	0.222	−16.935	0.185
286	9.8810	0.002286	−16.124	0.346	−15.778	0.217
290	16.062	0.002859	−15.618	0.566	−15.052	0.259
294	26.688	0.003488	−14.628	0.945	−13.683	0.287
298	43.916	0.004193	−13.192	1.562	−11.630	0.294
302	69.683	0.004989	−12.267	2.491	−9.776	0.294
306	105.18	0.005827	−11.365	3.778	−7.587	0.266
310	151.7	0.006609	−10.487	5.477	−5.010	0.200
314	214.41	0.007230	−9.6315	7.779	−1.853	0.0809
318	311.12	0.007438	−8.7973	11.346	2.5487	−0.114

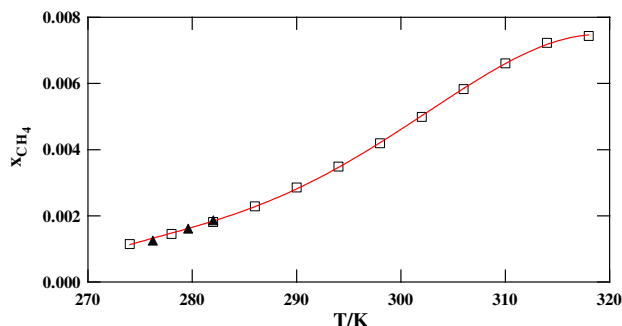


FIGURE 6. Mole fraction of CH_4 dissolved in water along the (liquid, hydrate, vapor) coexistence line. \square , calculated; \blacktriangle , measured by Servio and Englezos [28].

The second term in equation (A.3) is negligible since $V_{\text{CH}_4, \text{H}_2\text{O}}^{\infty}$ is almost independent of T . The fourth term in equation (A.3) is negligible due to the smallness of the water vapor pressure at the temperatures of hydrate formation. The other two terms can be evaluated using the results that we have presented above. Once $\Delta H_{\text{CH}_4, \text{H}_2\text{O}}^{\infty}$ is evaluated, it is multiplied by $-(nx_{\text{CH}_4}/(1 - x_{\text{CH}_4}))$ to find $\Delta H_{1\text{b}}$, the solubility correction term in the determination of ΔH_1 (see text). Although n is not known initially, a constant value of $n = 6.0$ can be used for this correction term with little error. The results are presented in table A.1. No error analysis is performed because $\Delta H_{1\text{b}}$ is small compared to ΔH_1 and thus contributes little error.

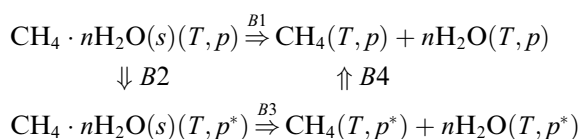
Appendix B. Correction of the enthalpy change of reaction (1) for temperature and pressure

To use equation (20) to calculate the hydration number, we must first convert the values of $\Delta H_1(T, p)$ to their effective values at the quadruple point Q1, where $p^* = 2.563 \text{ MPa}$ and $T^* = 272.9 \text{ K}$. We do this in two stages; first we correct for pressure, then temperature.

TABLE B.1
Values of ΔC_p^{av} vs. temperature for reaction (1)

T/K	ΔC_p^{av} ($\text{kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$)
274	0.232
278	0.229
282	0.227
286	0.225
290	0.223
294	0.221
298	0.219
302	0.217
306	0.215
310	0.213
314	0.211
318	0.209

The following thermodynamic cycle illustrates the correction for pressure.



$$\begin{aligned} \Delta H_1(T, p^*) &\equiv \Delta H_{B3} = \Delta H_{B1} - \Delta H_{B2} - \Delta H_{B4} = \\ &\Delta H_1(T, p) - [H_{\text{hyd}}(T, p^*) - H_{\text{hyd}}(T, p)] - \\ &[H_{\text{CH}_4}(T, p) - H_{\text{CH}_4}(T, p^*)] - \\ &n[H_{\text{H}_2\text{O}}(T, p) - H_{\text{H}_2\text{O}}(T, p^*)]. \end{aligned} \quad (\text{B.5})$$

The third and fourth terms in equation (B.5) are found from the equations of state of pure methane and water, respectively. For the second term, we use a form of the “thermodynamic equation of state”, valid for any substance,

$$\left(\frac{\partial H}{\partial p}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_p = V(1 - \beta T). \quad (\text{B.6})$$

The hydrate volume and thermal expansion coefficient β are reasonably constant, so to a good approximation,

$$H_{\text{hyd}}(T, p^*) - H_{\text{hyd}}(T, p) = V_{\text{hyd}}(1 - \beta T)(p^* - p) \quad (\text{B.7})$$

We use a similar thermodynamic cycle to correct ΔH_1 for temperature. The resulting equation is,

$$\Delta H_1^* \equiv \Delta H_1(T^*, p^*) = \Delta H_1(T, p^*) + \int_T^{T^*} \Delta C_p dT, \quad (\text{B.8})$$

where ΔC_p is the change of heat capacities between product and reactants. Handa [24] has measured the heat capacity of methane hydrate in the (ice, hydrate, vapor) region, from 85 K to 270 K. By extrapolation we can determine the values at temperatures in the LHV region. Combining this result with data for the heat capacities of water and methane, we can arrive

at an average value ΔC_p^{av} which simplifies equation (B.8).

$$\Delta H_1^* = \Delta H_1(T, p^*) + \Delta C_p^{\text{av}}(T^* - T). \quad (\text{B.9})$$

Table B.1 presents the ΔC_p^{av} values found by this procedure.

References

- [1] R. de Forcrand, Comptes Rendus 135 (1902) 959–961.
- [2] G. Anderson, J. Chem. Thermodyn. 35 (2003) 1171–1183.
- [3] E.D. Sloan Jr., Clathrate Hydrates of Natural Gases, second ed., Marcel Dekker, New York, 1998, pp. 314–318.
- [4] O.L. Roberts, E.R. Brownscombe, L.S. Howe, Oil Gas J. 39 (1940) 37.
- [5] B.J. Falabella, A Study of Natural Gas Hydrates, Dissertation, University of Massachusetts, Univ. Microfilms No. 76-5849, Ann Arbor MI, 1975.
- [6] W.M. Deaton, E.M. Frost Jr., US Bur. Mines Monograph 8 (1946).
- [7] T.Y. Makogon, E.D. Sloan, J. Chem. Eng. Data 39 (1994) 351.
- [8] A. Klapproth, E. Goreschnik, D. Staykova, H. Klein, W. Kuhs, Can. J. Phys. 81 (2003) 503–518.
- [9] P.J. Linstrom, W.G. Mallard, Eds. NIST Chemistry WebBook, NIST Standard Reference Database Number 69, July 2001, National Institute of Standards and Technology, Gaithersburg, MD 20899. Available from <http://webbook.nist.gov>.
- [10] D.R. Marshall, S. Saito, R. Kobayashi, AIChE J. 10 (1964) 202–205.
- [11] J. Jhaveri, D.B. Robinson, Can. J. Chem. Eng. 43 (1965) 75–78.
- [12] T.J. Galloway, W. Ruska, P.S. Chappellear, R. Kobayashi, Ind. Eng. Chem. Fundam. 9 (1970) 237–243.
- [13] R. Kobayashi, D.L. Katz, Trans. AIME 186 (1949) 66–70.
- [14] H.O. McLeod, J.M. Campbell, J. Petr. Tech. 222 (1961) 590.
- [15] V.K. Verma, Gas Hydrates from Liquid Hydrocarbon Systems, Dissertation, University of Michigan, Univ. Microfilms No. 75-10, Ann Arbor MI, 1974.
- [16] J.L. de Roo, C.J. Peters, R.N. Lichtenthaler, G.A. Diepen, AIChE J. 29 (1983) 651–657.
- [17] J.L. Thakore, G.D. Holder, Ind. Eng. Chem. Res. 26 (1987) 462–469.
- [18] S. Adisasmito, R.J. Frank III, E.D. Sloan Jr., J. Chem. Eng. Data 36 (1991) 68–71.
- [19] K.A. Udachin, C.I. Ratcliffe, J.A. Ripmeester, J. Phys. Chem. B 105 (2001) 4200–4204.
- [20] E.M. Frost, W.M. Deaton, Oil Gas J. 45 (1946) 170.
- [21] O.L. Roberts, E.R. Brownscombe, L.S. Howe, H. Ramser, Petr. Eng. 12 (1941) 56.
- [22] J.H. Yoon, Y. Yamamoto, T. Komai, H. Haneda, Ind. Eng. Chem. Res. 42 (2003) 1111–1114.
- [23] D. Glew, Can. J. Chem. 80 (2002) 418–439.
- [24] Y.P. Handa, J. Chem. Thermodyn. 18 (1986) 915–921.
- [25] I.R. Krichevsky, J.S. Kasarnovsky, J. Am. Chem. Soc. 57 (1935) 2168–2171.
- [26] A. Dhima, J.C. Hemptinne, J. Jose, Ind. Eng. Chem. Res. 38 (1999) 3144–3161.
- [27] T.R. Rettich, Y.P. Handa, R. Battino, E. Wilhelm, J. Phys. Chem. 85 (1981) 3230–3237.
- [28] P. Servio, P. Englezos, J. Chem. Eng. Data 47 (2002) 87–90.
- [29] B.B. Benson, D. Krause Jr., J. Sol. Chem. 18 (1989) 803–821.
- [30] Weast, C. Robert, Handbook of Chemistry and Physics, 61st ed., CRC, Florida, 1981, p. F-1.